

CARDEROCK DIVISION
Naval Surface Warfare Center
West Bethesda, MD 20817-5700

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Survivability, Structures, and Materials Department
Technical Report

COPPER-NICKEL CLADDING ON STAINLESS STEEL

by

David A. Shifler

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Copper-nickel cladding on conventional and super-austenitic stainless steel has proved effective in reducing maintenance (from biofouling, reapplication of anti-fouling coatings, and corrosion) for various small ferries, tankers, and ships in Europe and North America for periods of up to 30 years. This technology may have potential benefits and applications for the U.S. Navy, but several issues such as corrosion, mechanical and structural properties need to be evaluated and resolved before the possibility of copper-nickel cladding can be considered for use in the Fleet.

Paints may not adhere on stainless steels as well as steels and may cause crevice corrosion of the stainless steel if the coating is compromised. Copper-nickel cladding of austenitic stainless steels may also offer some ballistic, non-magnetic, and electromagnetic signature advantages over current hull alloys and corrosion control technologies, but is not discussed in this report. The purpose of this study is to evaluate corrosion-related benefits/disadvantages of using copper-nickel cladding on stainless steel structures. This study evaluates (1) the fouling characteristics of 70/30 (UNS C71500) and 90/10 (UNS C70600) copper-nickel cladding as an antifoulant and as a potential replacement for antifoulant coatings, (2) the crevice corrosion resistance of copper-nickel alloys with AL6XN or cheaper grades of austenitic stainless steels, (3) the effects of galvanic corrosion of copper-nickel alloys coupled to AL6XN or other stainless steel alloys, (4) effects of copper-nickel cladding on fabrication, and (5) corrosion impact of Cu-Ni/SS clad bi-metallic structures.

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EXECUTIVE SUMMARY

Copper-nickel cladding on conventional and super-austenitic stainless steel has proved effective in reducing maintenance (from biofouling, reapplication of anti-fouling coatings, and corrosion) for various small ferries, tankers, and ships in Europe and North America for periods of up to 30 years. This technology may have potential benefits and applications for the U.S. Navy, but several issues such as corrosion, mechanical and structural properties need to be evaluated and resolved before the possibility of copper-nickel cladding can be considered for use in the Fleet. Paints may not adhere on stainless steels as well as steels and may cause crevice corrosion of the stainless steel if the coating is compromised. Copper-nickel cladding of austenitic stainless steels may also offer some ballistic, non-magnetic, and electromagnetic signature advantages over current hull alloys and corrosion control technologies, but is not discussed in this report.

The purpose of this study is to evaluate corrosion-related benefits/disadvantages of using copper-nickel cladding on stainless steel structures. This study evaluates (1) the fouling characteristics of 70/30 (UNS C71500) and 90/10 (UNS C70600) copper-nickel cladding as an antifoulant and as a potential replacement for antifoulant coatings, (2) the crevice corrosion resistance of copper-nickel alloys with AL6XN or cheaper grades of austenitic stainless steels, (3) the effects of galvanic corrosion of copper-nickel alloys coupled to AL6XN or other stainless steel alloys, (4) effects of copper-nickel cladding on fabrication, and (5) corrosion impact of Cu-Ni/SS clad bi-metallic structures.

ADMINISTRATIVE INFORMATION

The work described in this report was performed by the Corrosion Research and Engineering Branch (Code 613) in the Metals Division (Code 61) of the Survivability, Structures and Materials Department at the Naval Surface Warfare Center, Carderock Division (NSWCCD). Mr. Richard Hays is the Manager of the Corrosion Research and Engineering Branch. The work was performed as part of a task for the Office of Naval Research, Code 333 under Document Number N0001405WX30096.

INTRODUCTION

Copper-nickel alloys were developed specifically for seawater service over 50 years ago for piping and condenser systems [1]. The two main copper-nickel alloys used in marine service are 90/10 and 70/30 copper-nickel alloys (UNS C70600 and UNS C71500), respectively. Both alloys contain small additions of iron and manganese that provide a combination of erosion resistance and overall corrosion resistance. Table 1 shows the typical compositions of these alloys. Maximum levels of some elements in 90/10 or 70/30 copper-nickel alloys are defined because of their effects on hot ductility, hot workability, and weldability [1].

Both 90/10 and 70/30 copper-nickel alloys are readily welded by the common welding methods [2]. The corrosion resistance of weld deposits made by approved weld consumables and of the adjacent, heat affected zone in these alloys generally does not pose a problem, as may be the case in some other alloy systems. Although very rare, erosion corrosion coupled with possible galvanic corrosion of a 70/30 copper-nickel weld heat affected zone between 70/30 copper-nickel water piping sections has been observed. 70Cu/30Ni welding rod should be used for welding both copper-nickel alloys to avoid promoting anodic sites at the weld itself. The 90/10 alloy is normally welded with a 70Cu/30Ni welding consumable and provides a deposit which is galvanically slightly more noble than the base alloy. For welding copper-nickel to steel, Monel (65Ni/35Cu) alloy consumables should be used as they can tolerate more iron dilution from the steel than the 70-30 copper-nickel alloy consumables [1]. Table 2 lists the consumable specifications and compositions. Cladding should not affect fabrication of structures as long as proper materials are selected and suitable joining procedures are followed.

The corrosion product layers formed on Cu/Ni alloys exposed to seawater depend on the alloy and water composition. In unpolluted seawater, a loosely adherent porous cupric hydroxy-chloride ($\text{Cu}_2(\text{OH})_3\text{Cl}$) corrosion product scale forms over a thin, tightly adherent layer of cuprous oxide (Cu_2O) that increases corrosion resistance with increased exposure times [3,4]. The iron and nickel alloying constituents from the UNS C71500 or UNS C70600 alloys are concentrated in the inner portion of the porous corrosion product layer [5]. Iron, if present in solid solution, also increases the corrosion resistance of copper-nickel alloys by assisting in the formation of the protective film [6]. The initial corrosion rate of Cu-Ni alloys is relatively high

but quickly decreases as the oxide film and the corrosion product layers are formed. The general corrosion rates are 0.002-0.02 mm/yr (0.08 – 0.8 mpy) in natural seawater [7].

Initial exposure to clean, natural seawater is extremely important to provide long-term performance of copper-nickel alloys. The initial film forms in a few days, but takes 2-3 months to fully mature [8]. Temperature likely plays an influential role in the time that is required for scale maturity.

Both 90/10 and 70/30 are the primary commercial copper-nickel alloys and have been the alloys chosen for cladding of various small ferries and ships in Europe. This report attempts to: (1) define some potential materials problems and advantages from the open literature related to the use of these copper-nickel alloys for cladding Al6XN®¹ (referred to as UNS N08367 for the remainder of this report), (2) define strategies to control problems, and (3) identify what research or testing needs to be done to address some problem areas. The composition of UNS N08367 is listed in Table 1.

ENVIRONMENTAL EFFECTS ON COPPER-NICKEL ALLOYS

Crevice Corrosion

Crevice corrosion seldom occurs in Cu-Ni alloys and little data is published in the open literature about the phenomenon. When encountered, crevice corrosion tends to be derived from the formation of a metal ion concentration cell corrosion which is opposite of the phenomenon occurring in stainless steels [7]. Metal ions accumulate within the crevice and the crevice progressively becomes noble relative to the boldly exposed area around the mouth of the crevice. Dissolution occurs in the anodic, boldly exposed area adjacent to the crevice on surfaces exposed to oxygenated bulk sea water and tends to be shallow. Water velocity can aggravate crevice attack, although penetration rates are unlikely to be severe. A break in the copper-nickel cladding would tend to cathodically protect the stainless steel alloys such as UNS N08367. Copper-nickel alloys likely will not crevice corrode when in contact with UNS N08367 alloy due to the specific mechanism of forming a metal ion concentration cell.

¹ Registered Trademark of the Allegheny Ludlum Corporation, Pittsburgh, PA

Dealloying

Copper-nickel alloys may be susceptible to dealloying, but it is not common. Denickelification has been observed in copper-nickel alloys when hot spots have developed due to formation of deposits on condensers above 150 °C [1]. The formation of deposits leads to hot spots that promote thermogalvanic couples with normally cooled piping. Such conditions would not be expected to exist for copper-nickel sheathing clad to UNS N08367 or any other hull material.

Environmentally Induced Cracking

Copper-nickel alloys are not susceptible to chloride or sulfide-induced stress corrosion cracking. 90/10 and 70/30 copper-nickel alloys are also not susceptible to hydrogen embrittlement or to cracking from ammonia in seawater. Ammonia may accelerate corrosion rates of copper-nickel alloys; 70/30 copper-nickel displays lower corrosion than 90/10 copper-nickel [1].

Sulfide Pitting

Hack and Gudas [9] showed that 90/10 Cu-Ni was susceptible to sulfide induced pitting in natural, flowing seawater containing 0.01 ppm or more sulfides. 70/30 Cu-Ni was similarly susceptible to sulfide-induced pitting but required higher sulfide (0.05 ppm) concentrations. Sulfide modified films generally were more loosely adherent than the normal cuprous oxide films; turbulence tended to selectively remove the sulfide-modified films. The exposed surfaces are anodic to the surfaces covered by the films and localized corrosion at the exposed sites is promoted. Depending on water quality, additional sulfide-modified films may form and the process becomes cyclic.

The measured corrosion potentials of 90/10 and 70/30 Cu-Ni alloys with sulfide modified films shifted to more noble (electropositive) values relative to 90/10 and 70/30 copper-nickel alloys with the normal $\text{Cu}_2(\text{OH})_3\text{Cl}$ and Cu_2O corrosion product films [9-11]. The magnitude of the noble potential shift tended to increase, in aerated flowing seawater, with increasing sulfide content or longer exposures times [9]. This electropositive potential shift was attributed to the chemical modification of the normal, protective films and pitting by galvanic interaction between the sulfide-modified films and freshly exposed Cu-Ni surfaces. The ease by which sulfide-modified films are removed supports the electrochemical/mechanical nature of pitting on Cu-Ni

alloys [9]. Later, it was considered that the electropositive shifts caused the sulfide modified Cu_2O film to break down locally and promote pitting at these sites.

Syrett *et al.* observed that the presence of sulfides interfered with the formation of normal passivating films of Cu-Ni alloys found in unpolluted waters. Instead, black, porous, nonprotective cuprous sulfide films were formed [12,13]. Sulfide exposure in deaerated seawater does not cause accelerated attack [14], but rather forms a duplex structure of a thin oxide-rich surface film covered with a thick cuprous sulfide scale [13]. The accelerated corrosion rates in aerated sulfide-containing seawater remain high since the sulfides prevent protective corrosion product layers to form [15]. The corrosion rate of Cu-Ni alloys during subsequent exposures to aerated, non-polluted seawater would remain high until the sulfide modified films either spalled or were removed.

Sulfide pollution can occur in several ways: (1) bacterial reduction of naturally occurring sulfates in seawater; (2) rotting vegetation; and (3) industrial waste discharge. Exposure of new 90/10 Cu-Ni samples exposed to putrid seawater for 24 hours produced pitting up to 0.007-in. deep and a corrosion rate of 0.038 in./yr. [10]. Monitoring of dockside waters of shipbuilding facilities revealed a background sulfide level of 0.01 ppm with periodic sulfide level excursions up to 0.27 ppm [10]. Bacterial contamination interferes with the normal passivation process of copper base alloys observed in unpolluted seawater [16].

The degree of sulfide-induced corrosion of Cu-Ni alloys can be reduced and controlled if the Cu_2O passive film is formed prior to exposure to polluted waters [11,15]. Pre-exposure of 90/10 and 70/30 Cu-Ni alloys to clean flowing seawater for a period of 120 days provided nearly total protection from sulfide-induced attack in polluted seawater containing 0.2 mg/L (0.2 ppm) sulfides for up to 15 days [11]. This was due to the formation of the Cu_2O film. However, pre-exposures of Cu-Ni alloys for 30 days in clean, flowing seawater were insufficient to provide complete resistance to subsequent sulfide attack [11].

Sulfide-induced pitting of copper-nickel alloys when used as sheathing for ship hulls should not occur if the ships are not left in port for long periods of time (> 6 months). The sulfide film should not develop under constant hydrodynamic flow present along the hull when the ship is operational.

Biofouling Resistance

Copper-nickel alloys have very good resistance to biofouling, and this property is used to advantage. The use of 90/10 copper-nickel, and to a lesser extent 70/30 copper-nickel, have antifouling characteristics and erosion corrosion properties that are superior to most other copper alloys [17,18].

Copper-nickel alloys have been used to minimize biofouling on intake screens, sea water piping systems, water boxes, cladding of pilings and mesh cages in fish farming. A prime example of this was in 1987 when two early copper-nickel hulled vessels, the *Asperida II* (54-foot yacht launched in 1968 consisting of 70/30 copper-nickel plate to a copper-nickel frame) and the *Copper Mariner* (67-foot shrimp boat operating off of Mexico and Nicaragua), were located after being in service for 21 and 16 years, respectively. Neither vessel required hull cleaning or had suffered significant hull corrosion during that time [19]. Copper-nickel has tended to be placed on steel hulls by cladding, welding or using adhesive-backed foil for small boats [19,20]. The *Copper Mariner II* (a 76-foot shrimp boat launched in 1983) incorporated a composite 90/10 copper-nickel plate 0.078-inch thick metallurgically bonded to steel and operated off the western coast of Mexico. After five years the owner stated that the hull had kept free from fouling and corrosion [19].

A cost analysis study using 90/10 copper-nickel for ship hulls was conducted on larger ships and compared to other antifouling technologies such as conventional antifouling paint and using a self-polishing co-polymer [18].

The antifouling technologies were installed and tested on two ship types: (1) a roll on/roll off vessel *Westward Venture* operating between Tacoma, WA and Cook Inlet, AK and (2) a crude oil carrier *Mobil Magnolia* operating between Rotterdam, Holland and Ras Tanura, Arabia Gulf [18]. The cost of the installation for conventional paint, self-polishing co-polymer, and copper-nickel sheathing was estimated to be 1:2:7.5, respectively, though the cost of copper-nickel could be reduced if weld process development was done. The ship characteristics are listed in Table 4. Though there were no specific indications of the panel locations, it is assumed that the panels were immersed, at least under the waterline for "light loads" since analysis of the three antifouling technologies measured the increase of drag due to an increase in surface roughness.

Using a roughness parameter for hull surfaces established by the British Ship Research Association, the Mean Apparent Amplitudes {MAA (incorporating the initial roughness, the roughness of the coating system, roughness caused by corrosion under the coating, and the roughness of the biofouling accumulated over a unit length of time)} of the three antifouling systems were assessed over an assumed remaining 16-year lifetime. The MAA measured at the initiation of the study occurred four years after the 3 antifouling systems had been applied; the MAA were 16.5 mils, 7.5 mils, and 2.5 mils for the conventional paint, self-polishing co-polymer, and 0.100-inch thick 90/10 copper-nickel sheathing, respectively. The roughness values for the remaining 16-year lifetime were 24.5 mils, 13.5 mils, and 4.5 mils for the conventional paint, self-polishing co-polymer, and 90/10 copper-nickel, respectively. Frictional resistance of the hull accounts for 50 percent or more of the total resistance for medium and slow-speed vessel which leading to a reduction in vessel speed and increased fuel consumption. The required freight rate (RFR) required to break even (using the amount of freight transported per year and the amount of fuel required for transporting the commodities per year) clearly showed that copper nickel sheathing was the most economical choice as an antifoulant in this study [18].

The *Arco Texas*, (91,000 DWT, 15.5 knots average vessel speed) had 4 groups of 90/10 copper-nickel panels (10 ft x 3ft each) installed below the "light load line" in 1981 and were compared to antifouling paint and self-polishing co-polymers [17]. Therefore the panels were continuously immersed in water even under the "light loads". Alternate wet/dry and splash zone conditions also were experienced [21]. The *Arco Texas* was in continuous service for 18 months and made seven trips through the Panama Canal. After the Canal crossings, the tanker was dedicated to the Alaska-Washington and Alaska-California routes. The panel attachment methods were: (1) 100 percent peripheral weld plus epoxy adhesive, (2) 100 percent peripheral weld only, (3) 100 percent peripheral weld plus elastomer, and (4) 100 percent peripheral weld plus slot welds. All welding was done by the shielded metal-arc welding process (SMAW). The panels were inspected five times over an eighteen month period. After eighteen months the average roughness for the copper-nickel panels and painted steel hulls were 61 microns (2.4 mils) and 370 microns (14.6 mils), respectively. Due to rubbing and bumping in the locks when traversing the Panama Canal, the painted antifoulant was extensively abraded and in some hull areas, completely peeled off. Conversely, the copper-nickel sheathing displayed a few scratches,

but was completely intact. If the entire hull had been sheathed in copper-nickel, it was estimated that the fuel consumption would have been decreased by about 20 percent [21].

Early theories of the biofouling resistance of copper-based alloys were based solely on the release of copper ions into seawater which are toxic to macrofouling. In general, the natural corrosion process of copper alloys can be subdivided into primary and secondary reactions [20]. During the primary reaction, a cuprous oxide film is formed. The anodic part of the reaction takes place at the metal/oxide interface and the cathodic part at the water/oxide interface. Since the cuprous oxide film does not represent a completely dense layer, the copper-nickel alloy continuously releases small amounts of copper ions. Because the ions cannot be tolerated by many organisms, such an ionic discharge is capable of decelerating the establishment of the primary bacterial film considerably. The required corrosion rate of 90-10 copper-nickel for fouling control is well below $25 \mu\text{m/y}$ (1 mpy), which is the usual corrosion rate of this alloy in marine environments [22].

However more recent studies have modified the early theories [22,23]. The biofouling depends on a freely corroding state [23]. Efirid considered that it was the surface film, itself, which was inhospitable to biofouling [24]. The toxic-ion-being-released-into-sea-water theory was further disputed by Efirid based on tests he carried out on 90-10 samples half-coated with nontoxic paint over a period of 24 weeks. If leaching of copper ions was the phenomenon, some protection of the nontoxic surface would also occur. Because it was found that, after extended time periods, the copper-nickel alloys tend to alternately lose and gain their fouling resistance, Efirid concluded that the film is duplex in nature. It was thought that the initial cuprous oxide film is resistant, but when it oxidizes after extended exposure to form a green cupric hydroxychloride, fouling seems to increase. Because the second film is not very adherent, it can be easily removed, preventing secure attachment. Once sloughed off, the exposed surface is resistant again.

The corrosion rate of copper-nickels will decrease with exposure time, but will vary somewhat depending on the specific exposure. Figure 1 show the decreasing rates of 90/10 copper-nickel based on its exposure to quiet, flowing (0.6 m/s) and tidal seawater [25,26]. In quiet seawater the corrosion rate of 90/10 copper-nickel was $4 \mu\text{m}$ per year after one year of exposure and $1.2 \mu\text{m}$ per year after 14 years of exposure [25,26]. In flowing seawater the

corrosion rate is 13 μm per year after one year and about 1.8 μm per year after 14 years while in tidal seawater the corrosion rate is 3 μm after one year and 1.6 μm after 14 years of continuous exposure [25-27].

If copper-nickel is cathodically protected, however, the biofouling resistance can be decreased. Optimal biofouling resistance also requires copper-nickel alloys to be electrically isolated from less noble alloys and free of cathodic protection [7,28].

During a test where 90/10 and 70/30 copper-nickel plates were immersed from a floating dock at Wrightsville Beach, NC very little fouling was apparent after 18 months, apart from the formation of slimes on both alloys. However, after five years, fouling covered about 2/3 of the respective copper alloy surfaces [25,27]. The fouling included tunicates, bryozoa, and serpulliads [27]. The biofouling was not strongly adherent; it could be removed by light scraping action and was observed to slough off periodically. On boat hulls, experience suggests that self-cleaning action exists when service velocities of 3-8 knots are reached to remove accumulated biofouling attached during extended moorings [26]. Several other publications speak about the experiences of using copper-nickel sheathing or foil on a variety of boats, ships, and vessels [29-32].

Velocity Effects

Removal of the corrosion product layer by excessive flow velocities leads to increased corrosion rates. Corrosion rates are often dependent on fluid flow and the availability of appropriate species required to drive electrochemical reactions. An increase in fluid flow may increase corrosion rates by removing protective films or increasing the diffusion or migration of deleterious species. Conversely, increased flow may decrease corrosion rates by eliminating aggressive ion concentration or enhancing passivation or inhibition by transporting the protective species to the fluid/metal interface.

Erosion-corrosion is associated with the flow-induced mechanical removal of a protective surface film that results in subsequent corrosion enhancement through electrochemical or chemical processes. It often has been considered that a critical fluid velocity related to the impacted material must be exceeded, but the velocity is not single valued; temperature, fluid (i.e. seawater) composition, geometry, and pipe diameter can affect maximum design velocity. Fluid velocity imposes disruptive shear stresses or pressure variations on the material surface or the

protective surface film. Erosion-corrosion may be enhanced by particles (solids or gas bubbles) and impact in multi-phase flows. Copper-based alloys are susceptible to a critical surface shear stress in seawater where the corrosion product film begins to breakdown and be removed from the alloy surface thereby initiating accelerated attack [33]. The accepted maximum velocities in unpolluted seawater for 90/10 and 70/30 copper-nickel in piping systems are 10-12 feet/sec (3.0-3.6 m/sec) and 15 feet/sec (4.6 m/sec) [34], although the actual critical velocity in smaller diameter piping is lower than the critical velocity of large (≥ 6 inches) piping.

In any given velocity domain, local velocity variations may exist over diverse areas of a component due to factors such as geometry, flow disruptions, or mode of fabrication [35]. Turbulent flow increases agitation of waters with the structural materials more than in laminar flow and tends to exacerbate erosion-corrosion and other forms of flow-related corrosion.

Most of the literature concerning effects of flow on copper-nickel alloys has involved piping applications. Yet, the hydrodynamics of ship hulls are different than the flow characteristics present within piping systems because of the changes in the fluid dynamic boundary layer growth. It would be expected that higher flow velocities can be tolerated for copper-nickel alloys applied on ship hulls than are observed in piping systems. Experience to date has shown minimal corrosion of 90/10 copper-nickel alloy on a ship hull after 14 months at 24 knots (12 m/s) [36]. The highest recorded velocity without measurable thickness loss of 90/10 copper-nickel cladding for 200 hours has been 38 knots (19 m/s) for a patrol boat operating at maximum speed [37]. The upper service velocity for copper-nickel alloys in conjunction its use on ship hulls has not been established [1].

Galvanic Corrosion

The necessary conditions for galvanic corrosion require: (1) dissimilar alloys, (2) electrical contact, either directly or by a secondary, grounding path, between the dissimilar alloys, and (3) an electrolyte. The coupling of dissimilar alloys in conducting, corrosive solutions such as seawater, oil and gas, and biological fluids can lead to accelerated corrosion of the more anodic, electronegative alloy and protection of the more cathodic, electropositive alloy. In general, the extent of galvanic corrosion depends on factors such as: (1) the type of joint; (2) the effective area ratio of the anodic and cathodic members of the galvanic couple; (3) geometry of the coupling members; (4) mass transport (convection, migration, and/or diffusion); (5) bulk solution

properties (oxygen content, pH, conductivity, pollutant/contamination level); (6) temperature; (7) flow rate; (8) volume of solution; (9) major and minor alloy constituents; (10) protective film characteristics (oxide, salt films, etc.) in the given environment; (11) surface condition; (12) reaction kinetics (metal dissolution of the anodic member, and either oxygen reduction or hydrogen evolution overvoltages, or the cathodic efficiency of the more noble, cathodic alloy); and (13) the difference in potential between the alloys [38,39]. Figure 2 shows these and other factors that affect galvanic corrosion [38]. If UNS N08367 and either 90/10 or 70/30 copper-nickel are coupled in seawater, the superaustenitic stainless steel will be the cathode and the copper-nickel alloy be the anode. The use of copper-nickel cladding over UNS N08367 will not lead to galvanic corrosion of the copper-nickel alloy if the cladding is complete; however, galvanic corrosion of the copper-nickel alloy is possible if mechanical damage or design deficiencies cause a break or defect in the cladding so that the UNS N08367 alloy becomes boldly exposed to seawater and completes a conductive circuit with the copper alloys.

Usually galvanic couples involve electrolytes containing dissolved oxygen. When the galvanic current is limited by oxygen diffusion to the cathode, it is under cathodic control. Under this condition the galvanic current rate is directly proportional to the cathode area and independent of the anode area [40]. The relationship of current vs. cathode area is referred to as the catchment area principle; this principle illustrates that the anodic current density is inversely proportional to the anode area. Therefore, the area of the cathode should be minimized so that the cathode/anode area ratio is very small for better long term performance. If the ship composed of UNS N08367 alloy is clad with a copper-nickel alloy, the cathode-to-anode ratio will be favorable to minimizing galvanic corrosion unless the cladding layer is breached. Then the magnitude of galvanic currents will depend on surface conditions and the area of the superaustenitic stainless steel actually exposed to the electrolyte.

The reaction rate of the cathodic oxygen reduction reaction as a function of hull velocity is not completely known. However, it would eventually be diffusion-limited based on the specific dissolved oxygen concentration in operational waters of the ship. If the copper-nickel cladding layer was breached, the cathode-to-anode (stainless steel to copper-nickel) area ratio would favor minimal galvanic corrosion of the copper-nickel alloy because of the relatively large copper-nickel surface area and the high electrical conductivity of seawater.

The composition of the electrolyte influences the magnitude, the distribution, and often the direction of the galvanic current flow. High-conductivity fluids such as natural seawater tend to spread out the galvanic currents over larger surface areas while low conductivity fluids will limit the galvanic current distribution to just the cathode/anode junction [41]. There could be slight variations in the solution conductivity depending on concentration of dissolved solids. Table 3 shows the variability of dissolved solids around the world. The presence of contaminants such as sulfides can vastly change the kinetics of galvanic corrosion by affecting the polarization responses of alloys when immersed in polluted seawater as shown in Figure 3 [42].

The magnitude of the potential difference between the dissimilar materials found in the galvanic series cannot predict the degree of galvanic corrosion because potentials are a function of the thermodynamics and cannot predict the reaction kinetics. A difference of 50 mV between select dissimilar materials can lead to severe corrosion while dissimilar materials with a potential difference of 800 mV have been successfully coupled [43]. Figure 4 shows the Galvanic Series in seawater at ambient temperature. The potential difference between the copper-nickel alloys and UNS N08367 is approximately 200 mV, yet it will depend on specific surface oxide films and conditions as to what the actual galvanic currents that will be generated. For example, when passive oxide film-forming alloys such as stainless steels, Cr-Ni-Mo alloys, and titanium are exposed in seawater, these alloys can exhibit a wide potential range in seawater. The electrochemical potential of high alloy stainless steels can vary by over 1000 mV depending on whether the alloy is immersed in deaerated seawater, natural seawater, hot seawater, or chlorinated seawater [43]. Depending on specific areas of operation and surface parameters, ship alloys could be effectively exposed to all conditions but chlorinated seawater. If superaustenitic stainless steels such as UNS N08367 were exposed at a breach in the copper-nickel cladding, the effective potential variations at the stainless steel surface would likely be cathodically controlled by the very large remaining copper-nickel alloy area in highly conductive seawater. It is unknown what the critical cathode-to-anode ratio (UNS N08367 to 90/10 or 70/30 copper-nickel area ratio) would be for a shift from anodic control to cathodic control before the copper alloys would suffer significant corrosion rates.

In general, when dissimilar alloys are coupled, the rate of dissolution at the anode or the reduction reaction at the cathode is not equal for all metals and alloys in a given environment. It is the reaction rate that occurs at the anode or cathode surface that determines the efficiency and

it varies from one alloy to another. Polarization caused by current flow between the dissimilar metals/alloys cause a shift in the electrochemical potential of the anodic alloy to a more electropositive value and the cathodic member to a more electronegative value in an attempt to reach the same overall potential for both members. The difference in potential between the anodic and cathodic members will be a result of the current and the electrolyte resistance. The extent of polarization will depend on the metal/alloy and the specific environment to which the galvanic couple is exposed. Generally, in neutral environments, the galvanic couple will be under cathodic control. The extent of cathodic polarization will determine how well a material will drive the corrosion of the anode. Highly polarizable alloys (alloys with low cathodic efficiency) will not tend to cause relatively severe galvanic corrosion. However, it must be noted that cathodic efficiency can change under different conditions that affect the material surface kinetics [43]. Galvanic relationships between different alloys may be altered in sulfide-polluted seawater [44] because this changes the stability of the passive films and the possible cathodic reactions.

Aluminum alloys, stainless steels, and titanium all have a stable oxide film and tend to polarize and hence, are poor cathodes. Nickel-base alloys such as Alloys 625, 686, C-276, and 59 will tend to be more efficient cathodes than aluminum alloys, stainless steels, and titanium. On the other hand, noble metals, such as platinum, silver, and copper, on which the naturally formed oxide films are very thin and are easily reduced to metal, act as efficient cathodes without polarizing and, therefore, tend to promote galvanic corrosion [43]. The increasing use of nonmetallic materials (metal-reinforced composites, graphite metal matrix composites, conducting polymers, semi-conducting metal oxides, and conducting inorganic compounds) often exhibit potentials that are more electropositive than most alloys, and when coupled to most alloys, cause galvanic corrosion [45]. Graphite is also very noble in aerated, near-neutral solutions and it forms no oxide film. Hence, graphite is also a very efficient cathode that has the potential to cause severe galvanic corrosion of many metals.

It was observed that 90/10 copper-nickel panels welded to hull steel did not appear to generate significant galvanic currents aboard the *Arco Texas* [17]. The vessel owner permitted the copper-nickel panels to remain after the 18-month test period, in large part because the panels performed better than expected.

In comparison to other potential cathode members of a galvanic couple, superaustenitic steels such as UNS N08367 will be a better cathode than a regular 300-series stainless steel, but will not be as effective as a cathode as a nickel-base alloy such as Alloy 625. In flowing, aerated seawater the oxide film is likely to thicken, thus diminishing bimetallic corrosion of the coupled metal even further, but cladding will prevent any films from forming as long the cladding layer is not compromised.

Galvanic Corrosion – Effects of the Environment

The galvanic corrosion rate of many copper and nickel-based alloys, and of stainless steels in seawater, depends upon the flow rate as well as the area ratio. Copper and copper-nickel alloys tend to become more noble, i.e., more electropositive, and corrode less as the flow rate increases. In well-aerated, flowing solutions nickel-based alloys and stainless steels are also likely to become more passive and corrode less than under stagnant conditions [43].

In general, the rate of corrosion of coupled and non-coupled metals decreases with exposure time. This is generally due to the diminishing rate of diffusion of oxygen (or hydrogen) through the corrosion product films at cathodic regions and corresponding protection afforded by the corrosion product at anodic sites. To some extent, therefore, the galvanic corrosion rate is affected by the permeability of the corrosion product. In seawater the alkaline conditions produced at the cathode may result in the formation of calcareous deposits.

Galvanic Corrosion – Mitigation Methods

There are several basic methods for mitigating galvanic corrosion: (1) selection of materials close to one another in the Galvanic Series; (2) change of environment; (3) breaking of the conductive path between the coupled alloys; (4) design of junctions to minimize crevices and promote advantageous geometry and area ratios; and (5) altering the respective overall cathodic or anodic reactions by coatings or cathodic protection [46].

The total cathodic and anodic currents must be equal i.e. $i_c A_c = i_a A_a$ where i_c and i_a are the current densities of the cathodic and anodic reactions respectively, and A_c and A_a are the cathodic and anodic areas. Coatings on the cathodic member are effective by promoting a more favorable cathodic to anode area ratio. In contrast, coatings of the anodic member of a galvanic

couple should be avoided because of unfavorable area ratios would accelerate corrosion of the anodic material if the coating develops holidays.

In very dilute electrolytes the extent of galvanic interaction is very narrow, but the pH changes in the thin boundary layer films at the couple are very dramatic. In a study looking at galvanic interactions between steel and zinc, the pH changes were confined to within 1.5 mm of the steel surface and ranged from a pH of 5.6 over the zinc area to 11.5 over the steel in quiescent 0.01 M NaCl [47]. As the conductivity of the solution increased, the effective area of interaction between the cathode and anode increased.

Cathodic protection has been used extensively in controlling corrosion in many environments. The use of rapid polarization has been routinely used for offshore structures in connection with cathodic protection systems because of formation of calcareous deposits that act as a natural coating and reduces current demand. Application of initially high current densities to steel resulted in the formation of very protective calcareous deposits in natural seawater [48-51]. The presence of calcareous deposits required lower maintenance and lower subsequent, long-term current densities than if lower current densities were first applied to the structures. Driving the potential of the more active alloy of the galvanic couple into its cathodic region controls galvanic corrosion.

Research was done over a period of two years to study various mitigation strategies to control galvanic corrosion effects of coupling a straight titanium alloy and Alloy 625 piping sections to straight 70:30 copper-nickel piping in flowing (at 6 fps (1.8 m/s)) seawater [52]. Both titanium and Alloy 625 pipes had similar cathodic potentials and generated similar galvanic current profiles when placed in similar piping configurations in contact with 70/30 copper-nickel. This is to be expected, as neither of these materials corrodes or has a thick protective film. Thus both should act as cathodes where the oxygen reduction occurs. Both uncoated titanium and Alloy 625 piping sections experienced ennoblement that caused an electropositive increase of several hundred millivolts on these noble alloys during a period between 14 and 65 days of exposure to natural seawater [52]. The galvanic currents increased 7-14 days after ennoblement occurred, indicating a probable cause/effect relationship of a threshold of potential difference between dissimilar alloys to generate a driving force for greatly increasing galvanic currents as shown in Figures 5 and 6. Figures 5 and 6 also show that Alloy 625 has greater

cathodic efficiency than titanium over exposure time, generating higher galvanic currents. Ennoblement of the cathode (titanium in this case) increased the potential difference between the anode and the cathode and this larger potential difference between the dissimilar alloys enhanced the driving force for increased galvanic corrosion of the more anodic, copper-nickel sections, Figure 7. The phenomenon of ennoblement is likely caused by microbial action that increases the cathodic kinetics and shifts the cathodic polarization curves to higher currents, thus increasing galvanic currents on the anode [53-56]. It is also observed during the over 600-day exposure that the galvanic currents and the potentials of both the cathode and the anode varied in flowing natural seawater [52]. The general trend was that the electrochemical potential of the cathode and the resulting galvanic current decreased with longer exposure times. This was due to the generation of thicker films which caused a slower reaction rate at the cathode, and decreased cathodic efficiency.

Galvanic compatibility of a copper-nickel alloy, MARINEL™, was tested with martensitic Type 416 (UNS S41600), austenitic Type 316 (UNS S31600) and compared to FERRALUM superduplex (UNS S32550) stainless steels in natural seawater [57]. The MARINEL™ composition is listed in Table 1. The copper-nickel to stainless steel area ratios tested were 1:1 and 1:10, respectively. In the absence of localized corrosion of the martensitic and austenitic stainless steels, the stainless steel was the cathodic component of the galvanic couple with copper-nickel. However, both 416 martensitic steel (UNS S41600) and 316 austenitic stainless steel (UNS S31600) experience pitting/crevice corrosion, and when that occurred, "polarity reversal" occurred and the copper-nickel (along with the superduplex stainless steel) was protected equally when the austenitic and martensitic stainless steels experienced localized corrosion. The current densities were $22.39 \pm 1.24 \mu\text{A}/\text{cm}^2$ and $20.49 \pm 2.92 \mu\text{A}/\text{cm}^2$, respectively when coupled to 416 martensitic stainless steel. In the absence of localized corrosion of 416 and 316 stainless steels, factors such as ennoblement and breakdown of the of the oxide layers on the copper-nickel alloy determined the extent of galvanic corrosion. Films formed under flowing conditions tended to be more protective than films formed under static conditions. However, flow may have removed these films and returned the copper-nickel alloy to high corrosion rates.

The possible exposure of a superaustenitic stainless steel such as UNS N08367 to seawater caused by mechanical damage of the copper-nickel sheathing will cause some accelerated corrosion of the copper-nickel alloy. UNS N08367, having higher resistance to localized corrosion than either UNS S41600 or UNS S31600 stainless steel alloys, will promote galvanic corrosion of copper-nickel alloys when coupled to these nonferrous alloys. However, the unfavorable area ratio (large copper-nickel anode vs. small UNS N08367 cathode) will likely limit the corrosion and be limited by oxygen diffusion. Increased velocity will promote increased oxygen to the site, but decreased boundary layer thickness will counter the rate of oxygen diffusion. Testing will confirm these predictions.

SUMMARY AND RECOMMENDATIONS

There is a lack of specific information on the corrosion behavior of 90/10 and 70/30 copper-nickel alloys when coupled to superaustenitic stainless steels alloys such as UNS N08367. There are specific welding procedures for copper-nickel alloys when welding to ferrous based alloys, but no specifications were found for welding copper-nickel to UNS N08367 at this time. Copper-nickel alloys likely will not crevice corrode when in contact with UNS N08367 due to the specific mechanism (metal ion concentration cell) by which copper-based alloys crevice corrode. Copper-nickel alloys can provide good biofouling control, but cathodic protection will negate these beneficial effects if employed; if cathodic protection is used, the copper-nickel sheathing would have to be electrically isolated from the CP system. Isolation would be impractical for copper-nickel cladding on ship hulls.

There are several areas that need to be studied further:

- Hull repair by welding processes could induce hot cracking of UNS N08367 due to exposure to copper. There is a need to evaluate and recommend practical solutions to avoid hot cracking.
- Cathodic protection will void the antifouling characteristics of copper-nickel alloys. Although this may reduce electromagnetic signatures, there may be other materials that are exposed to seawater associated with the underwater hull such as propellers that may still require cathodic protection. This needs to be evaluated.

- If copper-nickel sheathing or cladding is to be considered for use for the U.S. Navy, it must show long-term efficacy for fouling control in service environments (underway in warm and cold climates under blue ocean and littoral settings) and dockside (in unpolluted and polluted waters).
- In order that copper-nickel be considered as a viable option for the Navy, test samples produced per MIL-PRF-24647D (panel testing in semi-tropical and tropical environments) and copper release rate data from methods such as ASTM D6442 (90-days minimum) are recommended for testing. The panels should include a copper ablative system from the NAVSEA Qualified Product List as baseline to performance.
- A patch test on a ship with the duty-cycle and typical steaming pattern/rigorous environment (where rigorous fouling is known to occur) of a Navy surface combatant is highly recommended.
- Breaks in the copper-nickel cladding on UNS N08367 may promote corrosion. The effects of exposing UNS N08367 at breaks in the cladding needs to be studied in more detail in natural seawater as a function of temperature, velocity, sulfide content, salt content, and relative UNS N08367 to 90/10 or to 70/30 copper-nickel area ratios.

REFERENCES

1. C.A. Powell, H.T. Michels, "Copper-Nickel Alloys for Seawater Corrosion Resistance and Antifouling – A State of the Art Review", **CORROSION/2000**, paper 00627, NACE International, Houston, TX (2000).
2. Copper-Nickel Fabrication, NiDI/CDA/CDA Inc. Joint Technical Publication, NiDI Publication 12014, CDA Publication 139, Copper Development Association Inc. Publication A7020 (1999).
3. H.P. Hack, H. Shih, H.W. Pickering, "Role of the Corrosion Product Film in the Corrosion Protection of Cu-Ni Alloys in Saltwater", Surfaces, Inhibition, and Passivation, E. McCafferty and J. Brodd, eds., Proceedings Volume 86-7, The Electrochemical Society, Pennington, NJ, 355 (1986).
4. H.P. Hack, "Role of the Corrosion Product Film in the Corrosion Protection of Cu-Ni Alloys in Saltwater", DTNSRDC SME-87-22, CarderockDiv, Naval Surface Warfare Center, (November 1987).
5. C. Kato, J.E. Castle, B.G. Ateya, H.W. Pickering, "On the Mechanism of Corrosion of Cu-9.4Ni-1.7Fe in Air Saturated Aqueous NaCl Solution", J. Electrochemical Society, **127**, 1897 (1980).

6. C. Pearson, "Role of Iron in the Inhibition of Corrosion of Marine Heat Exchangers", *British Corrosion Journal*, **7**, 61 (1972).
7. "The Application of Copper-Nickel Alloys in Marine Systems", CDA Inc. Seminar-Technical Report 7044-1919 (1996).
8. A – A. Tuthill, "guidelines for the Use of Copper Alloys in Seawater", Nickel Development Institute (NIDI) Publication 12003, (1988).
9. J.P. Gudas, H.P. Hack, "Sulfide Induced Corrosion of Copper-Nickel Alloys", *Corrosion*, **35**, 67 (1979).
10. J.P. Gudas, G.J. Danek, R.B. Niederberger, "Accelerated Corrosion of Copper-Nickel Alloys in Polluted Waters", **CORROSION/76**, paper 76, NACE International, Houston, TX (1976).
11. H.P. Hack, J. P Gudas, "Inhibition of Sulfide-Induced Corrosion by Clean Water Preexposure", DTNSRDC/SME-79-85 (November, 1979).
12. D.D. MacDonald, B.C. Syrett, S.S. Wing, "The Corrosion of Cu-Ni Alloys 706 and 715 in Flowing Sea Water. II – Effect of Dissolved Sulfide", *Corrosion*, **35**, 367 (1979).
13. B.C. Syrett, "The Mechanism of Accelerated Corrosion of Copper-Nickel Alloys in Sulfide-Polluted Seawater", *Corrosion Science*, **21**, 187 (1981).
14. B.C. Syrett, S.S. Wing, "Effect of Flow on Corrosion of Copper-Nickel Alloys in Aerated Sea Water and in Sulfide-Polluted Sea Water", *Corrosion*, **36**, 73 (1980).
15. L.E. Eiselstein, B.C. Syrett, S.S. Wing, R.D. Caligiuri, "The Accelerated Corrosion of Cu-Ni Alloys in Sulfide-Polluted Seawater: Mechanism No. 2", *Corrosion Science*, **23**, 223, (1983).
16. D.J. Schiffrin, S.R. De Sanchez, "The Effect of Pollutants and Bacterial Microfouling on the Corrosion of Copper Base Alloys in Seawater", *Corrosion*, **41**, 31 (1985).
17. L.W. Sandor, "The Use of Copper-Nickel in Shipbuilding: A Status Report", *Naval Engineers Journal*, 147-153 (July 1985).
18. D.W. Czimmek, L.W. Sandor, "Economic and Technical Feasibility of Copper-Nickel Sheathing of Ship Hulls", *Marine Technology*, **22** (2), 142-154 (1985).
19. "Copper-Nickel Hulled Boats Around the World, From New York to Genoa, are Free of Fouling", Copper Topic No. 63, Copper Development Association, Inc. (Winter 1988).
20. W. Schleich, K. Steinkamp, "Biofouling Resistance of Cupronickel – Basics and Experience", Stainless Steel World 2003 Conference, Maastricht (November 2003).
21. C.A. Powell, "Copper Nickel Boat Hulls", Copper Development Association, New York, NY, http://www.copper.org/applications/cuni/txt_hulls.html, (July 2005)
22. F.A. LaQue, W.F. Clapp, "Relationships Between Corrosion and Fouling of Copper-Nickel Alloys in Seawater", *Trans. Electrochem. Soc.*, **87**, 103 (1945).
23. K. T. Jackson. "Biofouling and Corrosion Testing at AMTE, Langstone Harbour." IMI Yorkshire Alloys Ltd. Unpublished report. 1991.
24. K.D. Efird, "The Interrelation of Corrosion and Fouling of Metals in Seawater", *Materials Performance*, **15** (4), 16-25 (1976).

25. K.D. Eifird, D.B. Anderson, "Seawater Corrosion of 90/10 and 70/30 Copper-Nickel Alloys – 14 Years Exposures", *Materials Performance*, **33**(1), 3 (1975).
26. C.A. Powell, "Preventing Biofouling with Copper-Nickel", Publication 157 (October 2002).
27. C.A. Powell, "Biofouling, Section 1: Copper-Nickel Alloys – Resistance to Corrosion and Biofouling", Nickel Development Institute, <http://64.90.169.191/applications/marine/1-biofouling.html>
28. "Preventing Biofouling with Copper Alloys", CDA Publication 113, p.4 (July 1995).
29. L.H. Boulton, C.A. Powell, W.B. Hudson, "Aspects of Biofouling and Corrosion on Ship Hulls Clad with Copper-Nickel", Corrosion and Prevention-99, Sydney (October 1999).
30. S. Campbell, R. Fletcher, C.A. Powell, "Long-term Exposure Trials Evaluating the Biofouling and Corrosion Resistance of Copper-nickel Alloy Sheathing Materials", 12th International Congress on Marine Corrosion and Fouling, University of Southampton, UK (27-30 July 2004).
31. C. Powell, "Corrosion and Biofouling Resistance Evaluation of 90/10 Copper-Nickel", Eurocorr 2004, European Federation of Corrosion, Nice (September 2004).
32. H.T Michels, K.P. Geremia, "The Asperida, Copper-Nickel Sailboat after More than Thirty Years in Seawater", paper 05238, **CORROSION/2005**, NACE International, Houston, TX (2005).
33. K.D. Eifird, "Effect of Fluid Dynamics on the Corrosion of Copper-Based Alloys in Seawater", *Corrosion*, **33** (1), 3, (1977).
34. N.W. Polan, "Corrosion of Copper and Copper Alloys" in Corrosion, v. 13, ASM Handbook, ASM International, Materials Park, OH, 624 (1987).
35. G.J. Danek, "The Effect of Seawater Velocity on Corrosion Behavior of Metals", *Naval Engineers J.*, **78**, 763 (1966).
36. "Copper-Nickel Sheathing Costing Study-Phase III", MA-RD Report-770-87026, U.S. Department of Transportation (August 1987).
37. T. Glover, "Copper-Nickel Alloys for the Construction of Ship and Boat Hulls", *British Corrosion Journal*, **17** (4), 155-158 (1982).
38. J. W. Oldfield, "Electrochemical Theory of Galvanic Corrosion," *Galvanic Corrosion*, H. P. Hack, ed., ASTM, West Conshocken, PA, 5-22, (1988).
39. R. Francis, "Galvanic Corrosion of High Alloy Stainless Steels in Sea Water," *British Corrosion Journal*, **29**, 53, (1994).
40. W.G. Whitman, R.P. Russell, *Industrial Engineering Chemistry*, **16**, 276 (1924).
41. M.J. Pryor, "Bimetallic Corrosion", *Corrosion: Metal/Environment Reactions*, vol. 1, 2nd Ed., L.L. Sheir, ed., Newnes-Butterworths, London, 1:192-214 (1976).
42. D.J. Astley, "Use of Microcomputer for Calculation of the distribution of Galvanic Corrosion and Cathodic Protection in Seawater Systems", *Galvanic Corrosion*, H. P. Hack, ed., ASTM, West Conshohocken, PA, 53-78, (1988).
43. R. Francis, *Galvanic Corrosion: A Practical Guide for Engineers*, NACE International, Houston, TX, 5-23 (2001).

44. H.P. Hack, "Galvanic Corrosion of Piping and Fitting Alloys in Sulfide-Modified Seawater", Galvanic Corrosion, STP 978, H. P. Hack, ed., ASTM, West Conshohocken, PA, 339, (1988).
45. X.G. Zhang, "Galvanic Corrosion" in Uhlig's Corrosion Handbook, R. W. Revie, Ed., John Wiley and Sons, New York, 154-160 (2000).
46. M. G. Fontana, Corrosion Engineering, 3rd ed., McGraw-Hill, New York, 48 (1986).
47. E. Tada, K. Sugawara, H. Kaneko, *Electrochimica Acta*, **49**, 1019-1026 (2004).
48. J.E. Finnegan, K. P. Fischer, "Calcareous Deposits: Calcium and Magnesium Ion Concentrations", **CORROSION/89**, 89581, NACE International, Houston, TX (1989).
49. K. P. Fischer, J. E. Finnegan, "Cathodic Polarization Behaviour of Steel in Seawater and the Protective Properties of the Calcareous Deposits", **CORROSION/89**, 89582, NACE International, Houston, TX. (1989).
50. J. S. Luo, R. U. Lee, T. Y. Chen, W. H. Hartt, S. W. Smith, "Formation of Calcareous Deposits Under Different Modes of Cathodic Polarization", *Corrosion*, **47**, p.189 (1991).
51. K. E. Mantel, W. H. Hartt, T. Y. Chen, "Substrate, Surface Finish, and Flow Rate Influences on Calcareous Deposit Structure", *Corrosion*, **48**, 489, (1992).
52. D.A. Shifler, "Advanced Measures to Control Galvanic Corrosion in Piping Systems", CARDIVNSWC-TR-61-99-18, (September 1999).
53. S. C. Dexter and G. Y. Gao, "Effect of Seawater Biofilms on Corrosion Potential and Oxygen Reduction of Stainless Steel", *Corrosion* **44**, 717 (1988).
54. M. Eashwar, S. Maruthamuthu, S. Sathiyarayanan, K. Balakrishnan, "The Ennoblement of Stainless Steels by Marine Biofilms: The Neutral pH and Passivity Enhancement Model", *Corrosion Science*, **37**, 1169 (1995).
55. J. P. LaFontaine, S.C. Dexter, "Effect of Marine Biofilm on Galvanic Corrosion", Proceedings of the 1997 Tri-Service Conference on Corrosion, Session 6, Tri-Service Committee on Corrosion, Wrightsville Beach, NC (November, 1997).
56. V. Scotto, M.E. Lai, "The Ennoblement of Stainless Steels in Seawater: A Likely Explanation Coming from the Field", *Corrosion Science*, **25**, 1007 (1998).
57. S.A. Campbell, G.J.W. Radford, C.D.S. Tuck, B.D. Barker, "Corrosion and Galvanic Compatibility Studies of a High Strength Copper-Nickel Alloy", *Corrosion*, **58** (1), 57-71 (2002).

Table 1 – Specified Compositions of Selected Copper-Nickel Alloys and AL6XN [1]

Alloy	Weight Percent Composition									
	Cu	Cr	Ni	Fe	Mn	Zn (max)	C (max)	Pb (max)	S (max)	Other
90/10 UNS C70600	Rem.	--	9.0- 11.0	1.0- 2.0	0.5- 1.0	0.5	0.05	0.02	0.02	--
70/30 UNS C71500	Rem.	--	29.0- 33.0	0.4- 1.0	0.5- 1.5	0.5	0.05	0.02	0.02	--
Marinel™	Rem.	0.30- 0.50	14.0- 20.0	0.60- 1.40	3.50- 5.50	0.20	0.05	0.02	0.15	Al 1.40- 2.00; Nb 0.50-1.00
	Cu	Cr	Ni	Fe	Mn	Si	C	Mo	S	Other
AL6XN™	0.75 max	20.0- 22.0	23.5- 25.5	Rem.	2.00 max	1.00 max	0.03	6.00- 7.00	0.030	0.18- 0.25N; 0.40P max

UNS C70600 and UNS C71500 compositions are specified by ASTM B122 “Copper-Nickel-Tin, Copper-Nickel-Zinc (Nickel Silver), and Copper-Nickel Alloy Plate, Sheet, Strip, and Rolled Bar”, ASTM International, West Conshohocken, PA, (2004).

Specification for Marinel+. Marinel is a registered trademark of Meighs Ltd., Campbell Road, Stoke on Trent, Staffordshire ST4 4ER, UK.

AL6XN (UNS N08367) is a registered trademark of Allegheny Ludlum Corp., Pittsburgh, PA

Table 2 – Welding Consumable Specifications and Composition

Type	AWS *	DIN**				
Covered Electrodes			Cu	Ni	Mn	Ti
70Cu- 30Ni	A5.6 ECuNi	EL-CuNi30Mn	67	30	1.8	0.15
65Ni- 30Cu	A5.11 ENiCu-7	EL-NiCu30Mn	30	63	3.5	0.2
Filler Wires						
70Cu- 30Ni	A5.7 ERCuNi	SG-CuNi30Fe	67	31	0.8	0.3
65Ni- 30Cu	A5.14 ERNiCu-7	SG- NiCu30MnTi	64	29	3.2	2.2

* AWS – standard consumables as specified by the American Welding Society

** DIN – standard consumables as specified by the Deutsches Institut für Normung e. V.

Table 3 – Total Solids in Seawater at Different Locations

Body of Water	Total Dissolved Solids, ppm
Baltic Sea	8,000
Caspian Sea	13,000
Black Sea	22,000
Caspian Sea	13,000
Atlantic Ocean	37,000
Mediterranean Sea	41,000
Arabian Sea	39,000-47,000
Dead Sea	260,000

Table 4 – Ship Characteristics of the *Westward Venture* and the *Mobil Magnolia*[18]

Characteristics	<i>Westward Venture</i>		<i>Mobil Magnolia</i>	
	Metric	English	Metric (m)	English (feet)
Overall Length	241.02 m	790.75 ft	339.6 m	1114.29 ft
Length between perpendiculars	223.65 m	733.75 ft	324.0 m	1063.00 ft
Beam, molded	28.04 m	92.00 ft	53.5 m	175.52 ft
Depth, molded	18.33 m	60.14 ft	28.0 m	91.86 ft
Draft, molded at summer freeboard	9.02 m	29.60 ft	21.8 m	71.51 ft
Displacement, at summer freeboard	34,474 t	33,931 LT	324,133 t	319,015 LT
Total deadweight, at summer freeboard	18,202 t	17,915 LT	287,821 t	282,900 LT
Light ship weight	16,272 t	16,016 LT	36,694 t	36,115 LT
Propulsion power, shp	30, 420	30,000	36,499	36,000
Normal service speed	23.0 knots	23.0 knots	15.4 knots	15.4 knots
Wetted Surface, at summer freeboard	7339 m ²	79,000 ft ²	26,477 m ²	285,000 ft ²

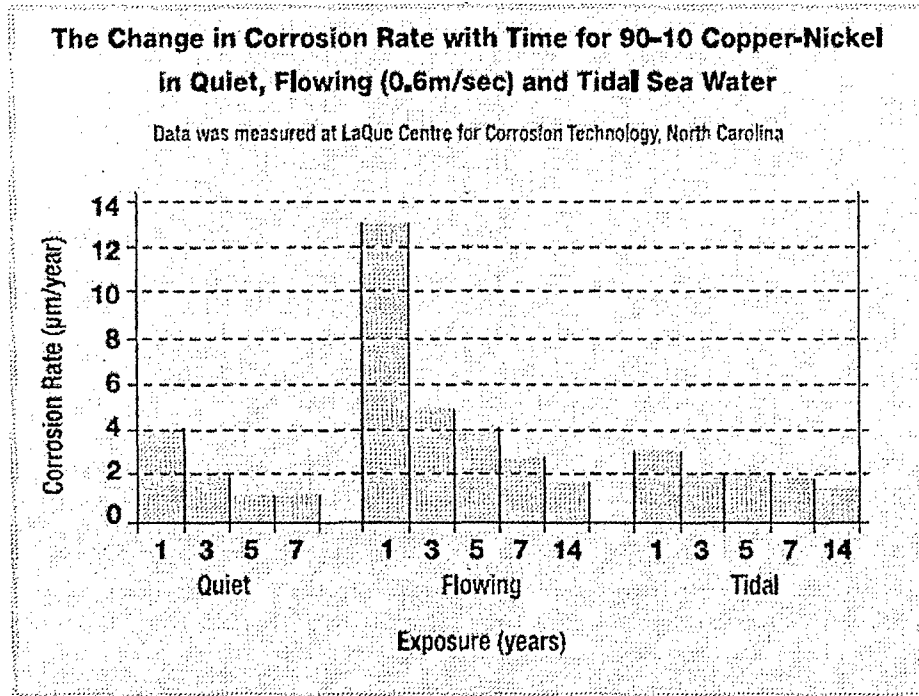


Figure 1 – Corrosion of 90/10 copper-nickel varies as a function of exposure and of time.

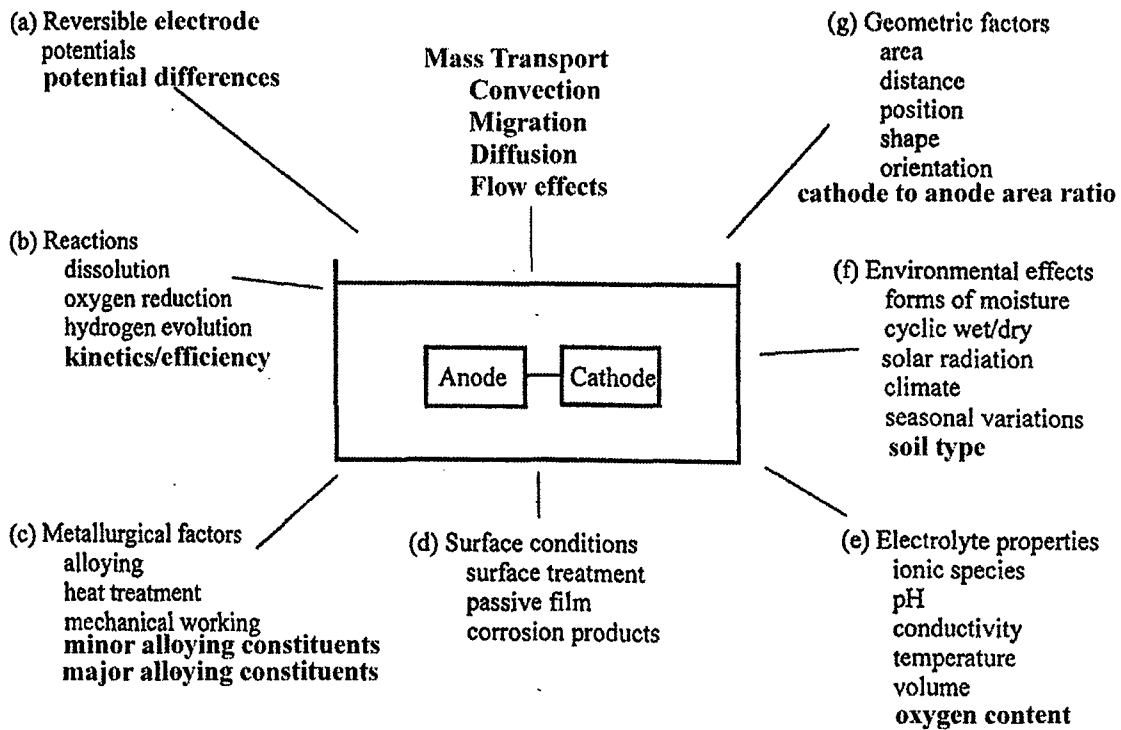


Figure 2 – Factors affecting galvanic corrosion.

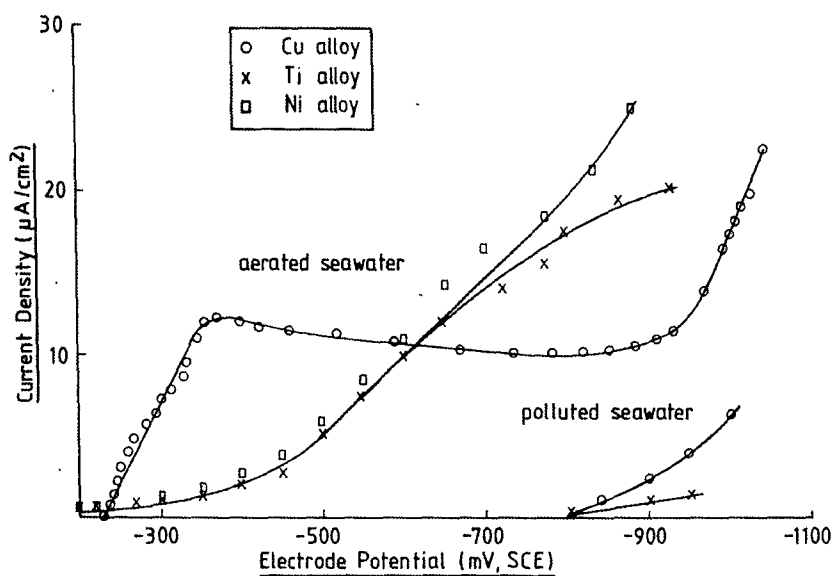
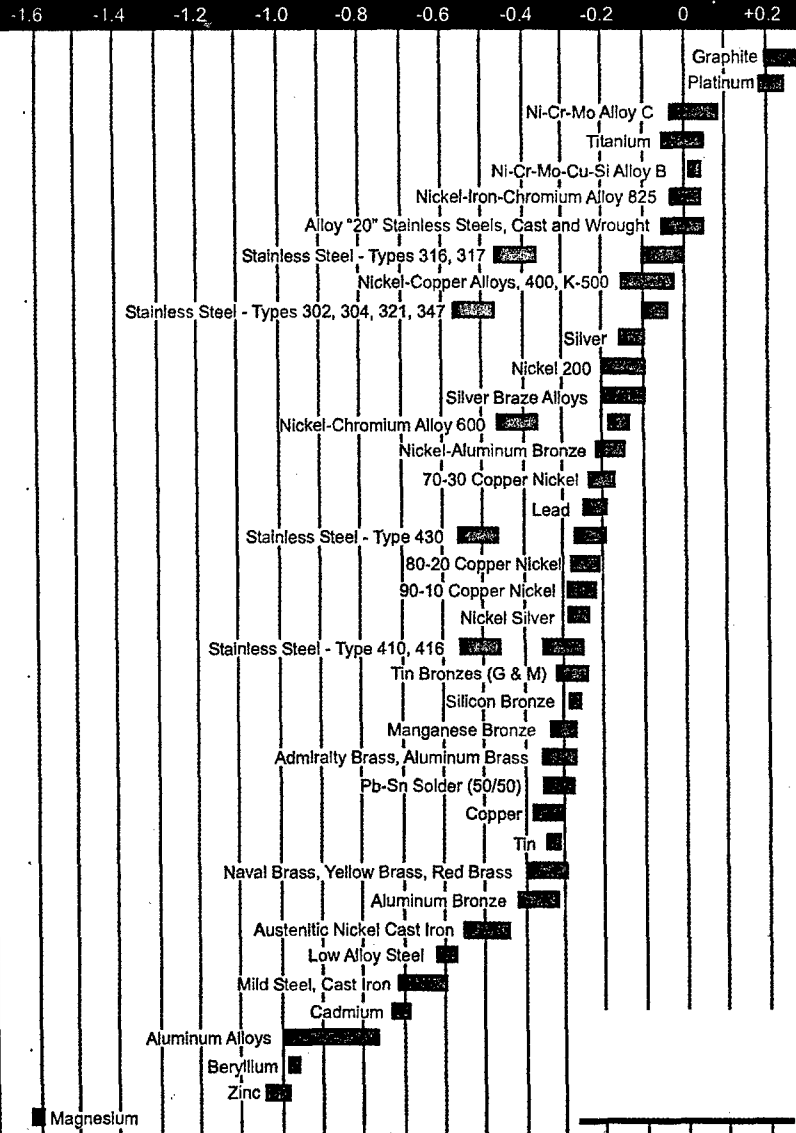


Figure 3 – Initial cathodic polarization curves for copper, titanium, and nickel alloys in aerated or in polluted seawater show distinct differences which could affect the reaction kinetics for galvanic corrosion.

GALVANIC SERIES

CORROSION - POTENTIALS IN FLOWING SEA WATER
(8 - 13 FT/SEC) TEMP. RANGE 50° - 80° F

VOLTS. SATURATED CALOMEL HALF CELL REFERENCE ELECTRODE



Source: Laque F.L., Marine Corrosion Causes & Prevention, John Wiley & Sons New York, NY 1975

Figure 4 – Galvanic series of several alloys in seawater at ambient temperatures. Arrows denote approximate potential ranges of UNS N08367 alloy and the respective copper-nickel alloys.

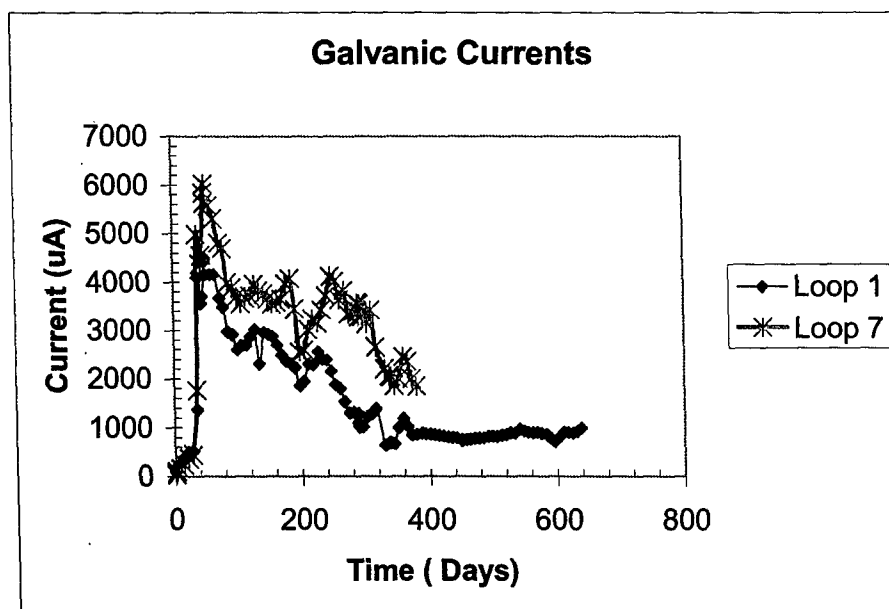


Figure 5 - Titanium/70:30 Copper-Nickel Piping Couples - measured galvanic currents per exposure time.

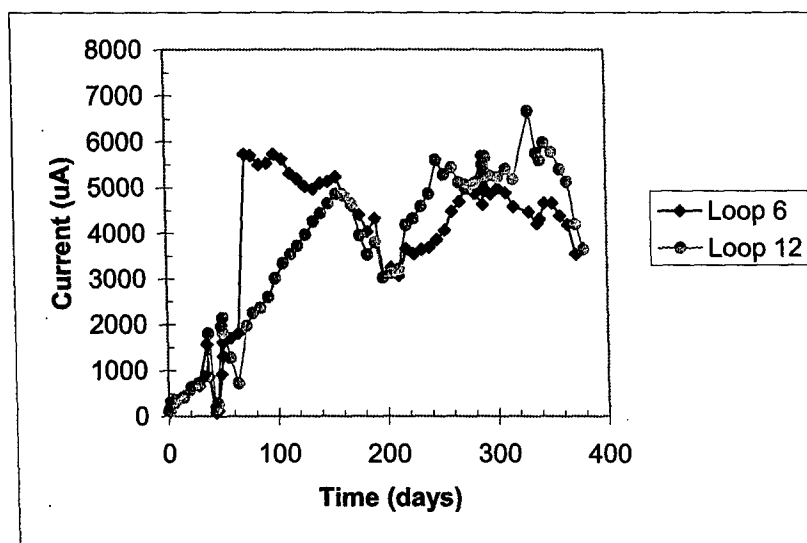


Figure 6 - Alloy 625/70:30 Copper-Nickel Piping Couples – measured galvanic currents as a function of exposure time.

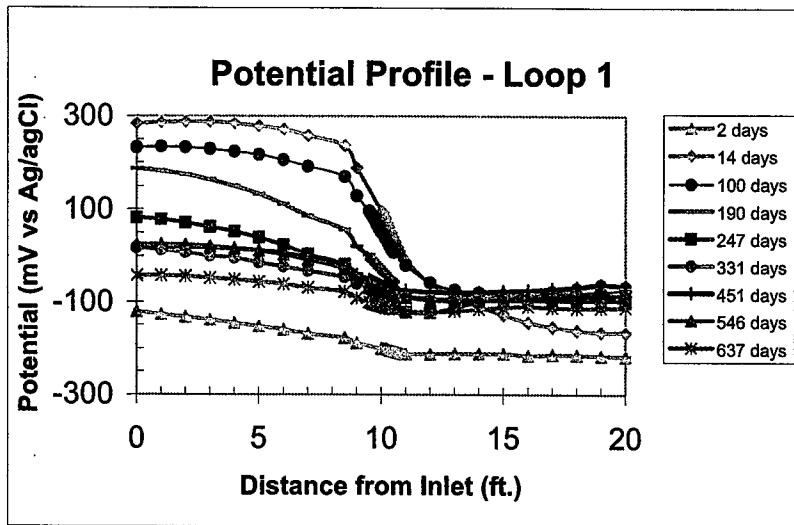


Figure 7 - Titanium/70:30 Copper-Nickel Piping Couple – potential profile of Loop No. 1 as a function of time.

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